

The Use of Diamond Electrodes for the Analytical Determination of Pentachlorophenol in Waters

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Electroanalytical methods are usually based on reduction processes occurring at a Hg surface. This electrode material has been widely employed due to the facility of surface renewal and the high hydrogen overpotential. Meanwhile, alternatives should be promptly seek to avoid the use of this and other electrodes made with heavy metals. On the other hand, voltammetric oxidations appear as an interesting tool in several cases.

Boron-doped Diamond (BDD) electrodes have received much attention in recent times due to its lack of reactivity as well as a very large electrochemical window that allows the use of extreme potentials without showing side reactions. Therefore, this material is an excellent candidate for the study of pentachlorophenol, an organo-chlorinated pesticide widely used in wood preservation^{1,2}.

This work reports the analytical determination of pentachlorophenol in pure and contaminated waters by square wave voltammetric oxidation on a BDD electrode.

Measurements were carried out in a mod.273A EG&G PARC potentiostat with the M270 software. A conventional three-electrode cell with a Ag/AgCl system and Pt wire as reference and auxiliary electrodes, respectively, was used. The working electrode was a 0.62 x 1.0 cm BDD single-faced plate gently provided by Dr. W. Hänni from CSEM, Neuchâtel, Switzerland. A 0.1 molL⁻¹ Britton-Robinson buffer with pH = 5.5 was used as the electrolyte and the pesticide was added from a 1 x 10⁻³ molL⁻¹ stock solution.

The effect of interferences was evaluated using water samples taken from a local creek at different points, namely, before (1), in the middle (2) and after crossing town (3). The measurements were performed without pre-treatment of the solutions but the pH was properly adjusted to 5.5.

Figure 1 shows the square wave voltammograms obtained for the oxidation of pentachlorophenol (PCP) at different concentrations taken after optimisation of the experimental parameters. A single oxidation peak is observed at ca. 0.82 V with E_p varying linearly with the logarithm of the square wave frequency (*f*). The relationship $\partial E_p / \partial \log f = 2.3RT / \alpha nF$ indicates that three electrons are involved in the oxidation of PCP.

Additionally, the linear relationship observed for the peak current with *f* suggests that the process is irreversible and involves adsorption of reagent and/or products. Those peak currents are also a linear function of the square wave amplitude up to 50 mV and remain constant afterwards. All these results are in agreement with the theoretical predictions applied to irreversible reactions with species adsorbed at the electrode surface³.

Figure 2 presents the analytical curves obtained by the standard addition method for concentrations of PCP varying from 0.1 to 6.0 x 10⁻⁵ molL⁻¹, in the different water samples.

The calculated detection limits (*DL*) are collected in Table I together with other relevant parameters and show how the presence of organic matter in the water sample increases considerably the *DL* value. This is probably due to blockage of the electrode surface by the organic molecules thus preventing the adsorption of the reagent. However, recovery experiments showed

efficiencies of the order of 95% regardless of the sample under investigation.

The results reported here demonstrate that the combination of square wave voltammetry and the Boron-doped Diamond electrode is a feasible alternative for the anodic determination of PCP and related molecules in either pure water or polluted natural matrixes.

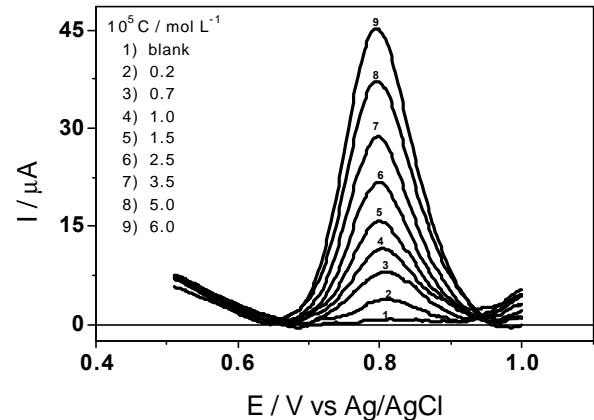


Figure 1 – Square wave voltammograms on BDD for PCP at various concentrations. *f* = 100 s⁻¹, Δ*E*_p = 50 mV, Δ*E*_s = 2 mV, pH = 5.5 (0.1 molL⁻¹ B-R buffer).

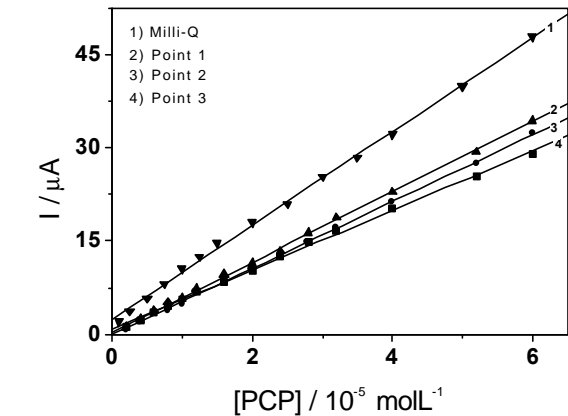


Figure 2 – Analytical curves for PCP in the different water samples. Other conditions as in Fig. 1.

Table I. – Detection Limit (*DL* = 3*S*_B / *b*) for the determination of PCP obtained by linear regression analysis of the curves in Fig. 2

Water sample	<i>R</i>	<i>S</i> _B (nA)	<i>B</i> (A/molL ⁻¹)	<i>DL</i> ppb
Milli-Q	0.9992	0.0163	0.760	17
Point 1	0.9996	0.0167	0.570	23
Point 2	0.9995	0.0173	0.540	25
Point 3	0.9989	0.0163	0.480	27

References

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2 - Sarada, B.V., *et al.*, *Anal. Chem.*, **72**, 1632-1638 (2000).
3 - Lovric, M., *et al.*, *J. Electroanal. Chem.*, **248**, 239-253 (1988).

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